Purification Strategies for Electron Beam Induced Deposition

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Electron beam induced deposition (EBID) is a direct-write process which can be used to selectively deposit precursor molecules onto a substrate with nanoscale resolution. Specifically, EBID utilizes a scanning focused electron beam to dissociate adsorbed precursor molecules which subsequently condense onto the substrate. One of the major limitations of the EBID process is low material purity resulting from incomplete by-product removal of the typically organometallic precursor. Therefore, the development of EBID purification strategies for enhanced materials functionality is a grand challenge for wider application of this technique.

Recently we have shown the viability of low temperature electron-beam-assisted oxygen purification for EBID Pt patterns deposited using $MeCpPt^{IV}Me^3$ precursor gas [1]. The electron stimulated reaction of oxygen molecules adsorbed on high-binding-energy sites of the deposit facilitates purification. Figure 1 shows the effects of oxygen temperature and pressure on deposit purification during electron beam irradiation. While optimal purification results were achieved with an oxygen temperature of 50^oC at a chamber pressure of $5.5x10^{-5}$ mbar, we will demonstrate improved efficiency at room temperature.

We have also demonstrated a laser assisted electron-beam-induced-deposition (LAEBID) process as an effective method to provide *in-situ* purification during deposition [2]. The synchronized process is initiated by an approximately monolayer EBID cycle followed by a laser pulse which thermally desorbs by-products of the condensed phase. The process is repeated until the desired shape and size is achieved. Figure 2 shows purification results for LAEBID Pt patterns. We will demonstrate how factors such as laser pulse width, EBID beam current, and EBID dwell time have significant effects of the subsequent deposition purification. Importantly, the carbon reduction and apparent densification lead to higher resolution relative to standard EBID.

Drawing from both strategies, we will finally discuss a new synchronized in-situ LAEBID process with reactive oxygen ambient as a combinatory purification strategy. During this procedure, EBID is performed using a co-flow of oxygen and MeCpPtIVMe3. After each EBID pass, a synchronized laser pulse irradiates the surface which thermally induces CO_x and purifies the deposit in-situ. The fully synchronized process will be overviewed and the specific electron-precursor-laser regimes will be elucidated.

[1] H. Plank, J.H. Noh, J.D. Fowlkes, K. Lester, B.B. Lewis, and P.D. Rack, ACS Appl. Mater. Interfaces 2014, **6**, 1018−1024.
[2] N.A. Roberts, J.D. Fowlkes, G.A. Magel, and P.D. Rack, Nanoscale, 2013, **5**, 408–415.

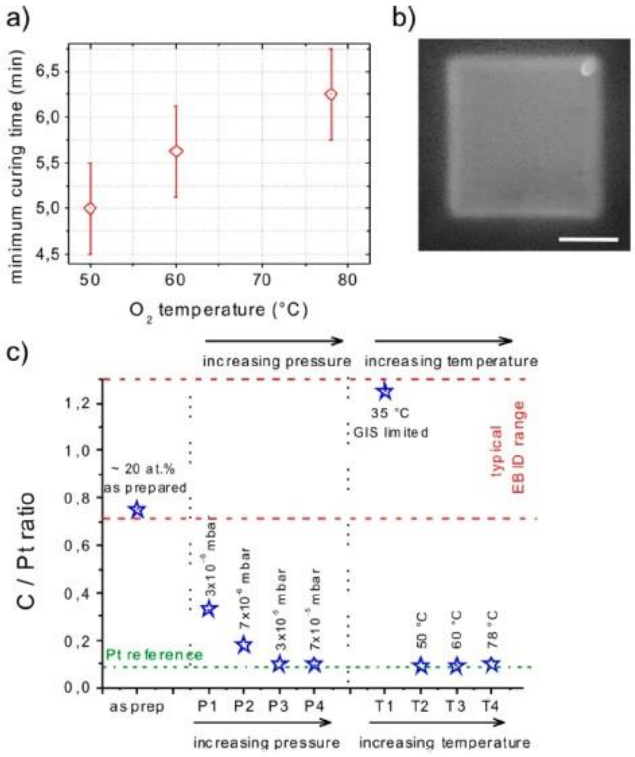

Figure 1. (a) Temperature dependence of the minimum purification times for a constant O2 pressure of 5.5 × 10−5 mbar. (b) SEM image of an initially 110 nm deposit, fully purified under optimal conditions of 50 °C O2 gas temperature at a pressure of 5.5 × 10−5 mbar, revealing a distortion-free morphology (scale bar is 200 nm). (c) Summary plot of C/Pt ratios at different relative to a Pt thin film reference (green bottom line).

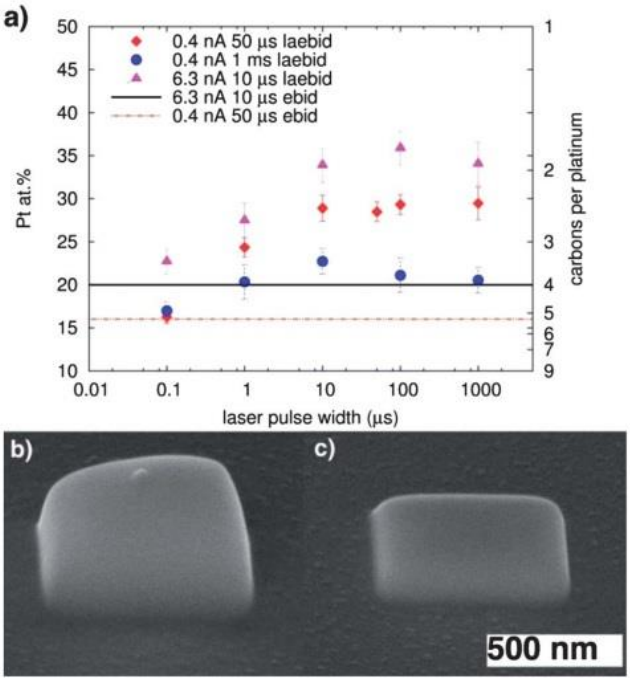

Figure 2. (a) Atomic concentration (and C/Pt ratio right axis) of platinum determined from the ratio of integrated platinum to integrated carbon peak from EDS spectra as a function of laser pulse width for different EBID conditions. SEM image of a (b)EBID platinum and (c) LAEBID platinum deposit.